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Published Version

### Peer-review status of attached file:

Peer-reviewed

### Citation for published item:

Teale, A.M. and De Proft, F. and Tozer, D.J. (2008) 'Orbital energies and negative electron affinities from density functional theory : insight from the integer discontinuity.', *Journal of chemical physics.*, 129 (4). 044110.

### Further information on publisher's website:

<http://dx.doi.org/10.1063/1.2961035>

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# Orbital energies and negative electron affinities from density functional theory: Insight from the integer discontinuity

Andrew M. Teale,<sup>1,3</sup> Frank De Proft,<sup>2</sup> and David J. Tozer<sup>3,a)</sup>

<sup>1</sup>*Centre for Theoretical and Computational Chemistry, Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo, Norway*

<sup>2</sup>*Eenheid Algemene Chemie (ALGC), Vrije Universiteit Brussel (VUB), Pleinlaan 2, 1050 Brussels, Belgium*

<sup>3</sup>*Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, United Kingdom*

(Received 7 May 2008; accepted 27 June 2008; published online 30 July 2008)

Orbital energies in Kohn–Sham density functional theory (DFT) are investigated, paying attention to the role of the integer discontinuity in the exact exchange–correlation potential. A series of closed-shell molecules are considered, comprising some that vertically bind an excess electron and others that do not. High-level *ab initio* electron densities are used to calculate accurate orbital energy differences,  $\Delta\epsilon$ , between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO), using the same potential for both. They are combined with accurate vertical ionization potentials,  $I^0$ , and electron affinities,  $A^0$ , to determine accurate “average” orbital energies. These are the orbital energies associated with an exchange–correlation potential that averages over a constant jump in the accurate potential, of magnitude  $\Delta_{XC} = (I^0 - A^0) - \Delta\epsilon$ , as given by the discontinuity analysis. Local functional HOMO energies are shown to be almost an order of magnitude closer to these average values than to  $-I^0$ , with typical discrepancies of just 0.02 a.u. For systems that do not bind an excess electron, this level of agreement is only achieved when  $A^0$  is set equal to the negative experimental affinity from electron transmission spectroscopy (ETS); it degrades notably when the zero ground state affinity is instead used. Analogous observations are made for the local functional LUMO energies, although the need to use the ETS affinities is less pronounced for systems where the ETS values are very negative. The application of an asymptotic correction recovers the preference, leading to *positive* LUMO energies (but bound orbitals) for these systems, consistent with the behavior of the average energies. The asymptotically corrected LUMO energies typically agree with the average values to within 0.02 a.u., comparable to that observed with the HOMOs. The study provides numerical support for the view that local functionals exhibit a near-average behavior based on a constant jump of magnitude  $\Delta_{XC}$ . It illustrates why a recently proposed DFT expression involving local functional frontier orbital energies and ionization potential yields reasonable estimates of negative ETS affinities and is consistent with earlier work on the failure of DFT for charge-transfer excited states. The near-average behavior of the exchange–correlation potential is explicitly illustrated for selected systems. The nature of hybrid functional orbital energies is also mentioned, and the results of the study are discussed in terms of the variation in electronic energy as a function of electron number. The nature of DFT orbital energies is of great importance in chemistry; this study contributes to the understanding of these quantities. © 2008 American Institute of Physics. [DOI: 10.1063/1.2961035]

## I. INTRODUCTION AND BACKGROUND

Kohn–Sham density functional theory (DFT) is the most widely used electronic structure method. Practical calculations rely on an accurate representation of the exchange–correlation energy and its functional derivative, the exchange–correlation potential  $v_{XC}(\mathbf{r})$ . Perdew *et al.*<sup>1</sup> demonstrated that a plot of the exact total electronic energy as a function of electron number comprises a series of straight line segments, with derivative discontinuities at the integers. This has the important consequence that the exact exchange–correlation potential jumps discontinuously as the electron number increases through an integer. The issue has attracted

significant recent interest.<sup>2–15</sup> In particular, Sagvolden and Perdew<sup>3</sup> re-examined the assumptions in the original proof. They concluded that the discontinuity is rigorously a constant jump for one-electron systems, and they established a strong presumption that it is a constant jump for many-electron systems. (A constant jump refers to a shift in the potential by the same amount at all points in space;<sup>3</sup> the value of the jump is both system and electron number dependent).

In the present study, we shall consider the implications of the integer discontinuity in practical DFT calculations using local functionals such as generalized gradient approximations (GGAs). We shall show that local functional frontier orbital energies are consistent with a potential that averages over a constant jump, the magnitude of which is given by the discontinuity analysis. The results will provide key insight

<sup>a)</sup>Author to whom correspondence should be addressed. FAX: +44 191 384 4737. Electronic mail: d.j.tozer@durham.ac.uk.

into the orbital energies of DFT, illustrating why they are so different from the Koopmans values.<sup>16,17</sup> The study will also provide justification and insight into a recently proposed DFT scheme<sup>9</sup> for estimating negative electron affinities. It also has direct relevance to other important aspects of DFT, including the failure of charge-transfer excited states<sup>10</sup> and the asymptotic breakdown of exchange-correlation potentials.<sup>18</sup>

We commence by summarizing the relevant theory; see Ref. 1 for full details. The linearity of the energy, combined with Janak's theorem,<sup>19</sup> leads to exact orbital energies for systems with  $N-f$  and  $N+f$  electrons of

$$\begin{aligned}\epsilon_N(N-f) &= -I^0, \\ \epsilon_{N+1}(N+f) &= -A^0,\end{aligned}\quad (1)$$

where  $0 < f < 1$  and  $I^0$  and  $A^0$  are the exact ground state vertical ionization potential and electron affinity, respectively, of the  $N$  electron system. In the limit  $f \rightarrow 0$ , the exact exchange-correlation potentials on the limiting electron deficient and electron abundant sides of the integer  $N$ , denoted as  $v_{XC}^-(\mathbf{r})$  and  $v_{XC}^+(\mathbf{r})$ , respectively, differ by the integer discontinuity,

$$\Delta_{XC} = v_{XC}^+(\mathbf{r}) - v_{XC}^-(\mathbf{r}), \quad (2)$$

where we have assumed a constant jump. In this limit, the orbital energies in Eq. (1) can be identified as the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of the  $N$ -electron system, determined using  $v_{XC}^-(\mathbf{r})$  and  $v_{XC}^+(\mathbf{r})$ , respectively. We therefore write the exact HOMO energy of the  $N$  electron system determined using  $v_{XC}^-$  as

$$\epsilon_{\text{HOMO}}^- = -I^0 \quad (3)$$

which implies that  $v_{XC}^-(\mathbf{r})$  vanishes asymptotically ( $\mathbf{r} \rightarrow \infty$ ).<sup>20,21</sup> We write the exact LUMO energy of the  $N$ -electron system determined using  $v_{XC}^+$  as

$$\epsilon_{\text{LUMO}}^+ = -A^0. \quad (4)$$

Equations (3) and (4) are exact Koopmans-type relationships for DFT.

The potential  $v_{XC}^-(\mathbf{r})$  differs from  $v_{XC}^+(\mathbf{r})$  by the spatial constant  $\Delta_{XC}$ , and so the orbital energies from the two potentials also differ by this amount; from Eqs. (2) and (4), the exact LUMO energy determined using  $v_{XC}^-$  is

$$\epsilon_{\text{LUMO}}^- = -A^0 - \Delta_{XC}, \quad (5)$$

and so combining Eqs. (3) and (5) gives the discontinuity<sup>22</sup>

$$\Delta_{XC} = (I^0 - A^0) - (\epsilon_{\text{LUMO}}^- - \epsilon_{\text{HOMO}}^-). \quad (6)$$

This is a key equation. The orbital energies  $\epsilon_{\text{LUMO}}^-$  and  $\epsilon_{\text{HOMO}}^-$  can be accurately calculated from *ab initio* electron densities, and so combining them with experimental  $I^0$  and  $A^0$  permits the calculation of accurate approximations to  $\Delta_{XC}$ .

Consider the implications of the integer discontinuity for practical approximate DFT calculations on systems containing integer  $N$  electrons. Perdew and Levy<sup>22</sup> presumed that local functionals—whose potentials are continuous with

electron number—approximately average over the discontinuity. We denote the exact average (av) potential by

$$v_{XC}^{\text{av}}(\mathbf{r}) = \frac{v_{XC}^-(\mathbf{r}) + v_{XC}^+(\mathbf{r})}{2} = v_{XC}^-(\mathbf{r}) + \frac{\Delta_{XC}}{2}, \quad (7)$$

which lies exactly midway between  $v_{XC}^-(\mathbf{r})$  and  $v_{XC}^+(\mathbf{r}) = v_{XC}^-(\mathbf{r}) + \Delta_{XC}$ , approaching the nonzero value  $\Delta_{XC}/2$  asymptotically. The corresponding orbital energies are

$$\epsilon_{\text{HOMO}}^{\text{av}} = -I^0 + \frac{\Delta_{XC}}{2} \quad (8)$$

and

$$\epsilon_{\text{LUMO}}^{\text{av}} = -A^0 - \frac{\Delta_{XC}}{2}, \quad (9)$$

and so

$$\epsilon_{\text{LUMO}}^{\text{av}} + \epsilon_{\text{HOMO}}^{\text{av}} = -(I^0 + A^0). \quad (10)$$

For open-shell systems in a restricted formalism, the HOMO and LUMO energies are degenerate, and the discontinuity in Eq. (6) reduces to  $I^0 - A^0$ . The average potential is then

$$v_{XC}^{\text{av}}(\mathbf{r}) = v_{XC}^-(\mathbf{r}) + \frac{I^0 - A^0}{2}, \quad (11)$$

and the HOMO and LUMO energies equal the negative of the electronegativity

$$\epsilon_{\text{HOMO}}^{\text{av}} = \epsilon_{\text{LUMO}}^{\text{av}} = -\frac{I^0 + A^0}{2}. \quad (12)$$

It is well established that open-shell HOMO energies from local functionals lie well above  $-I^0$ . They are much closer to the value in Eq. (12),<sup>22</sup> consistent with an exchange-correlation potential that approximately averages over the discontinuity in regions of space that are relevant to the HOMO. Of course, in asymptotic regions the average potential approaches a nonzero value, whereas the local functional potential vanishes. These regions of space are of little significance for the HOMO, and so its energy is barely affected by this breakdown; the more diffuse higher-lying orbitals are more affected. (The breakdown is easily repaired using an asymptotic correction (AC); we shall explicitly illustrate this in Sec. II, quantifying the influence on both the HOMO and LUMO energies. See Ref. 18 for further discussion).

In our own studies, we have provided further compelling evidence that the potentials of local functionals should, and do, approximately average over the integer discontinuity in open-shell systems. In Ref. 23, we demonstrated that for the open-shell atoms up to chlorine, the approximate homogeneity of a local functional (degree 4/3) requires its potential to resemble Eq. (11) if it is to yield accurate exchange-correlation energies and potentials simultaneously. In Ref. 24, we demonstrated that for the hydrogenic atoms H,  $\text{Li}^{2+}$ ,  $\text{C}^{5+}$ , and  $\text{O}^{7+}$ , the exchange-correlation potentials from a standard GGA functional closely resemble the average potential in Eq. (11) in nonasymptotic regions despite the fact that the shift (the hardness) varies by more than an order of magnitude between the systems. In our local functional de-

velopment work,<sup>20</sup> we have highlighted the need to add constant shifts of approximately  $(I^0 - A^0)/2$  in fits to open-shell accurate  $v_{\text{XC}}^-(\mathbf{r})$  potentials in order to obtain accurate energies and potentials simultaneously, again in accordance with Eq. (11).

All this evidence relates to open-shell systems, which are generally able to vertically bind the excess electron; i.e., the vertical electron affinity  $A^0$  is positive. In Ref. 9, evidence was provided that an approximate average behavior is also observed for  $\text{F}_2$  and  $\text{Cl}_2$ , which also have positive vertical affinities but which are closed shell systems. Most closed-shell systems, however, cannot vertically bind an excess electron. This issue was briefly considered by Sagvolden and Perdew,<sup>3</sup> who concluded that for the helium atom, the discontinuity may not be well defined. Nevertheless, it remains important to understand how local functionals behave for closed-shell systems and whether this behavior can be understood in terms of the above mathematical analysis.

As in the open-shell case, it is well known that closed-shell HOMO orbital energies lie well above  $-I^0$ , again suggesting a shift in the potential from  $v_{\text{XC}}^-(\mathbf{r})$  in regions of space that are relevant to the HOMO. To further quantify this, we considered in Ref. 25 a series of closed-shell molecules that do not vertically bind an excess electron. We used the Zhao–Morrison–Parr<sup>26</sup> (ZMP) procedure to determine accurate values of  $\epsilon_{\text{HOMO}}^-$  and  $\epsilon_{\text{LUMO}}^-$ , and we combined these with experimental ionization potentials and electron affinities to obtain values of the quantity  $\Delta_{\text{XC}}$  in Eq. (6). We then used these values to compute the average HOMO energies in Eq. (8) and compared them with HOMO energies from local functionals. The agreement was rather good, leading us to conclude that for these systems, the local functional HOMO energy is still consistent with the average potential in Eq. (7), as in the positive electron affinity case. The interesting feature of this earlier study is that in the evaluation of Eq. (6), we set  $A^0$  to be the *negative* experimental electron affinity from electron transmission spectroscopy<sup>27,28</sup> (ETS) rather than the ground state affinity, which is zero. The ETS affinity reflects the energy of the temporary anion (shape resonance) associated with the temporary electron capture in the LUMO; the ground state affinity reflects the true ground state energy of the anion, which equals that of the neutral due to loss of the excess electron (assuming no dipole-bound state).

Overall, therefore, studies suggest that local functionals yield orbital energies that are reasonably close to those in Eqs. (8) and (9), with  $\Delta_{\text{XC}}$  defined in Eq. (6), irrespective of whether the excess electron binds or not. In the former case,  $A^0$  is the positive ground state affinity. In the latter, defining  $A^0$  to be the negative ETS affinity appears to be the appropriate choice. In Ref. 10, we used this to provide insight into the failure of local functionals to describe long-range charge-transfer excitations. In Ref. 9, Tozer and De Proft (TDP) went further, suggesting that it could be used as a direct method for estimating electron affinities in closed-shell systems. Rearranging the approximate local functional analog of Eq. (10) and approximating  $I^0$  using a local functional gives their unconventional affinity expression,

$$A^{\text{TDP}} = -(\epsilon_{\text{LUMO}}^{\text{local}} + \epsilon_{\text{HOMO}}^{\text{local}}) - I^{\text{local}}. \quad (13)$$

Affinities determined in this manner are not quantitatively accurate. For systems where the electron binds, it cannot compete with affinities determined in the conventional manner,  $A = E_N - E_{N+1}$ . However, for systems where the electron does not bind, it does provide an estimate of the negative ETS affinity, which does not collapse to zero when the basis set becomes diffuse; this is the fundamental difficulty with the conventional approach. Negative affinities determined using Eq. (13) have been shown<sup>29</sup> to correlate well with the experimental ETS values, which is particularly important in conceptual DFT where chemical trends are central. Ejlsing and Nielsen<sup>30,31</sup> demonstrated that it can also be applied successfully to anionic species. More recently, it has been used to control the binding of the excess electron in temporary anions, allowing self-consistent calculations to be performed.<sup>32,33</sup>

The present study has three aims. The first is to review briefly our existing numerical evidence regarding the influence of the integer discontinuity on local functionals; this has been achieved in the preceding paragraphs. The second aim is to provide a thorough and coherent investigation into the nature of local functional frontier orbital energies in closed-shell systems in order to assess how well they can be understood in terms of the above mathematical analysis. In particular, we shall address a range of issues that have not been considered previously: (1) We shall consider both the average HOMO and LUMO energies and not just the former; (2) we shall consider the possibility of using the ETS and ground state (zero) affinities and not just the former; (3) we shall consider the possible breakdown of the LUMO energy due to the asymptotic breakdown of the exchange-correlation potential; (4) we shall separately consider systems that bind and do not bind an excess electron; (5) we shall explicitly plot the potentials to quantify the average behavior; and (6) we shall consider hybrid functionals, with reference to conventional and optimized effective potential calculations. The third and final aim is to provide justification and insight into the unconventional affinity expression in Eq. (13) and its ability to yield a qualitative description of the negative ETS affinity.

We commence in Sec. II by using high-level *ab initio* electron densities and accurate ionization potentials and electron affinities to determine accurate values of the average orbital energies in Eqs. (8) and (9). We then compare orbital energies from conventional local functionals with these average values, together with the Koopmans values. Exchange-correlation potentials of selected systems are explicitly presented. Orbital energies from hybrid functionals are also briefly considered, and the results of the study are discussed in terms of the variation in electronic energy as a function of electron number. Conclusions are presented in Sec. III. Calculations are performed using CADPAC (Ref. 34) and a development version of DALTON.<sup>35</sup>



TABLE I. Accurate<sup>a</sup> vertical ionization potentials and electron affinities (in a.u.).

Molecule	$I^0$	$A^{0,GS}$	$A^{0,ETS}$
Systems that do vertically bind an excess electron			
SO <sub>2</sub>	0.459	0.026	...
Cl <sub>2</sub>	0.422	0.022	...
F <sub>2</sub>	0.577	0.011	...
Systems that do not vertically bind an excess electron			
H <sub>2</sub> CO	0.401	0.000	-0.055
C <sub>2</sub> H <sub>4</sub>	0.392	0.000	-0.066
CO	0.515	0.000	-0.066
PH <sub>3</sub>	0.389	0.000	-0.070
H <sub>2</sub> S	0.386	0.000	-0.077
HCN	0.500	0.000	-0.085
HCl	0.469	0.000	-0.121
CO <sub>2</sub>	0.506	0.000	-0.140
NH <sub>3</sub>	0.398	0.000	-0.206
HF	0.592	0.000	-0.220
H <sub>2</sub> O	0.464	0.000	-0.235
CH <sub>4</sub>	0.526	0.000	-0.287

<sup>a</sup> $I^0$  and  $A^{0,ETS}$  are experimental values from Refs. 37 and 38, respectively;  $A^{0,GS}$  for SO<sub>2</sub>, Cl<sub>2</sub>, and F<sub>2</sub> are calculated using CCSD(T)/aug-cc-pVTZ.

## II. RESULTS AND DISCUSSION

### A. Accurate average orbital energies

We consider the 15 closed-shell molecules, SO<sub>2</sub>, Cl<sub>2</sub>, F<sub>2</sub>, H<sub>2</sub>CO, C<sub>2</sub>H<sub>4</sub>, CO, PH<sub>3</sub>, H<sub>2</sub>S, HCN, HCl, CO<sub>2</sub>, NH<sub>3</sub>, HF, H<sub>2</sub>O, and CH<sub>4</sub>, using the same near-experimental geometries of Ref. 36. Experimental vertical ionization potentials are available<sup>37</sup> for all these systems; the values are denoted as  $I^0$  in Table I. To confirm the validity of this choice of experimental data, we have also determined the ionization potentials using CCSD(T)/aug-cc-pVTZ. The values agree with the experimental ones to better than 0.1 eV on average. For the electron affinities, the first three molecules are known to have positive experimental adiabatic affinities, but we are not aware of experimental vertical affinities. It is well established that the remaining 12 molecules do not vertically bind an excess electron. To further investigate this, we have determined vertical affinities using CCSD(T)/aug-cc-pVTZ. For the first three molecules, positive values are obtained, indicating that the excess electron does bind. For the remaining 12 molecules, small negative values are obtained, reflecting the artificial binding of the excess electron by the finite basis set. The column of values denoted as  $A^{0,GS}$  in Table I therefore represents our best estimates of the true *ground state* (GS) vertical electron affinities. For the first three molecules, the values are the CCSD(T)/aug-cc-pVTZ affinities; for the remainder, they are zero because the ground state corresponds to the neutral plus a free electron, again assuming no dipole-bound states.

For the 12 molecules that do not bind an excess electron, we must also consider using the negative ETS affinities, which are usually quoted as being the “experimental” vertical affinities for these systems<sup>38</sup> and which are the appropriate quantities in conceptual DFT. The values, taken from Ref. 38, are denoted as  $A^{0,ETS}$  and are presented in Table I.

For each system, the Wu–Yang<sup>39</sup> (WY) approach was

applied to the CCSD(T)/aug-cc-pVTZ electron density; all calculations in this study use this basis set. Following Ref. 20, the WY exchange-correlation potential represents our best estimate to the exact electron deficient potential,

$$v_{XC}^{WY}(\mathbf{r}) \approx v_{XC}^{-}(\mathbf{r}), \quad (14)$$

while the WY orbital energies represent our best estimates to the corresponding exact orbital energies,

$$\begin{aligned} \epsilon_{HOMO}^{WY} &\approx \epsilon_{HOMO}^{-}, \\ \epsilon_{LUMO}^{WY} &\approx \epsilon_{LUMO}^{-}. \end{aligned} \quad (15)$$

The WY quantities are formally identical to those obtained using the ZMP procedure, and the WY HOMO orbital energy should be close to the negative of the experimental ionization potential,  $-I^0$  [Eq. (3)].

In the WY procedure, the exchange-correlation potential is expanded in terms of an auxiliary basis set; we choose to use the  $G_{large}$  basis set of Ref. 40, although in practice very similar results are obtained using the primary orbital basis. We use a standard reference potential containing the Fermi–Amaldi term in order to ensure an asymptotic  $-1/r$  behavior. Several studies highlighted the problem of unphysical potentials when the orbital and potential basis sets are unbalanced,<sup>40–43</sup> and we investigated several approaches to avoid such problems. First, we considered a truncated singular value decomposition,<sup>44</sup> as was done in Ref. 40. Next, we used the  $\lambda$ -regularization scheme of Bulat *et al.*,<sup>45</sup> defining the optimal  $\lambda$  from the corner of the  $L$ -curve or from the maximum in the reciprocal slope. Finally, we considered the alternative approach of choosing  $\lambda$  to minimize the absolute difference between the HOMO energy and  $-I^0$ ; the  $\lambda$  values from this final method were rather close to those using the other approaches. Investigations revealed that all four approaches gave very similar HOMO-LUMO gaps, which are the key quantities in the present study [see Eq. (6)]. For the present work, we therefore choose to use the final approach since this ensures not only that the gaps are accurate but also that unphysical shifts in the potentials and orbital energies are minimized. We reiterate that the gaps and thus the conclusions of this study are insensitive to this choice. The gaps are very close to those presented in Ref. 25, which used the alternative ZMP procedure.

The accurate WY gaps were used, in conjunction with the data in Table I, to calculate accurate values for the average HOMO and LUMO energies in Eqs. (8) and (9). Values determined using  $A^{0,GS}$  are denoted as

$$\epsilon_{HOMO}^{av,GS} = -I^0 + \frac{\Delta_{XC}^{GS}}{2} \quad (16)$$

and

$$\epsilon_{LUMO}^{av,GS} = -A^{0,GS} - \frac{\Delta_{XC}^{GS}}{2}, \quad (17)$$

where

$$\Delta_{XC}^{GS} = (I^0 - A^{0,GS}) - (\epsilon_{LUMO}^{WY} - \epsilon_{HOMO}^{WY}). \quad (18)$$

Those determined using  $A^{0,ETS}$  are denoted as

TABLE II. HOMO energies compared to  $-I^0$ . All quantities are in a.u.

Molecule	$\epsilon_{\text{HOMO}}^{\text{WY}}$	$\epsilon_{\text{HOMO}}^{\text{PBE}}$	$\epsilon_{\text{HOMO}}^{\text{PBE(AC)}}$	$\epsilon_{\text{HOMO}}^{\text{B3LYP}}$	$\epsilon_{\text{HOMO}}^{\text{av.GS}}$	$\epsilon_{\text{HOMO}}^{\text{av.ETS}}$	$-I^0$
Systems that do vertically bind an excess electron							
SO <sub>2</sub>	-0.448	-0.294	-0.293	-0.340	-0.312	...	-0.459
Cl <sub>2</sub>	-0.422	-0.268	-0.268	-0.308	-0.281	...	-0.422
F <sub>2</sub>	-0.560	-0.347	-0.342	-0.420	-0.365	...	-0.577
$ d $ vs $-I^0$	0.010	0.183	0.185	0.130			
$ d $ vs $\epsilon_{\text{HOMO}}^{\text{av.GS}}$	0.157	0.016	0.019	0.036			
Systems that do not vertically bind an excess electron							
H <sub>2</sub> CO	-0.399	-0.230	-0.225	-0.278	-0.272	-0.245	-0.401
C <sub>2</sub> H <sub>4</sub>	-0.392	-0.249	-0.245	-0.278	-0.302	-0.269	-0.392
CO	-0.513	-0.332	-0.330	-0.383	-0.390	-0.357	-0.515
PH <sub>3</sub>	-0.376	-0.247	-0.246	-0.279	-0.315	-0.280	-0.389
H <sub>2</sub> S	-0.383	-0.232	-0.231	-0.266	-0.302	-0.263	-0.386
HCN	-0.499	-0.332	-0.329	-0.370	-0.398	-0.356	-0.500
HCl	-0.468	-0.296	-0.295	-0.336	-0.371	-0.311	-0.469
CO <sub>2</sub>	-0.501	-0.334	-0.332	-0.381	-0.414	-0.344	-0.506
NH <sub>3</sub>	-0.398	-0.227	-0.221	-0.272	-0.315	-0.212	-0.398
HF	-0.586	-0.355	-0.345	-0.421	-0.483	-0.373	-0.592
H <sub>2</sub> O	-0.463	-0.266	-0.260	-0.321	-0.368	-0.251	-0.464
CH <sub>4</sub>	-0.525	-0.347	-0.343	-0.393	-0.447	-0.303	-0.526
$ d $ vs $-I^0$	0.003	0.174	0.178	0.130			
$ d $ vs $\epsilon_{\text{HOMO}}^{\text{av.GS}}$	0.094	0.078	0.081	0.034			
$ d $ vs $\epsilon_{\text{HOMO}}^{\text{av.ETS}}$	0.162	0.022	0.023	0.035			

$$\epsilon_{\text{HOMO}}^{\text{av.ETS}} = -I^0 + \frac{\Delta_{\text{XC}}^{\text{ETS}}}{2} \quad (19)$$

and

$$\epsilon_{\text{LUMO}}^{\text{av.ETS}} = -A^{0,\text{ETS}} - \frac{\Delta_{\text{XC}}^{\text{ETS}}}{2}, \quad (20)$$

where

$$\Delta_{\text{XC}}^{\text{ETS}} = (I^0 - A^{0,\text{ETS}}) - (\epsilon_{\text{LUMO}}^{\text{WY}} - \epsilon_{\text{HOMO}}^{\text{WY}}). \quad (21)$$

These average energies are now used to quantify the nature of local functional orbital energies.

## B. Orbital energies from a local functional

The first column of Table II lists the WY HOMO energies denoted as  $\epsilon_{\text{HOMO}}^{\text{WY}}$ . The second column lists HOMO energies from conventional Kohn–Sham calculations using the representative Perdew–Burke–Ernzerhof<sup>46</sup> (PBE) local functional denoted as  $\epsilon_{\text{HOMO}}^{\text{PBE}}$ . The final three columns list  $\epsilon_{\text{HOMO}}^{\text{av.GS}}$ ,  $\epsilon_{\text{HOMO}}^{\text{av.ETS}}$ , and  $-I^0$ . Mean absolute differences  $|d|$ , relative to the latter three quantities, are also presented for the two molecular subsets—those that bind an electron and those that do not. (The former subset is very small, reflecting the difficulty of finding closed-shell molecules with positive vertical affinities that are amenable to good quality WY calculations). For all 15 molecules, the  $\epsilon_{\text{HOMO}}^{\text{WY}}$  values are uniformly close to  $-I^0$ , with mean absolute differences of just 0.010 and 0.003 a.u. for the two subsets, reflecting the exact Koopmans relationship [Eq. (3)].

As has been widely observed, the  $\epsilon_{\text{HOMO}}^{\text{PBE}}$  values are uniformly above  $-I^0$  by averages of 0.183 and 0.174 a.u. for the two subsets. For the first three molecules, which do bind an excess electron, the  $\epsilon_{\text{HOMO}}^{\text{PBE}}$  values are, however, significantly

closer to the average orbital energy,  $\epsilon_{\text{HOMO}}^{\text{av.GS}}$ , with a mean absolute difference of just 0.016 a.u. For the remaining molecules, which do not bind an excess electron,  $\epsilon_{\text{HOMO}}^{\text{PBE}}$  and  $\epsilon_{\text{HOMO}}^{\text{av.GS}}$  do not agree as well—the mean absolute difference is almost five times greater at 0.078 a.u. However, consistent with Ref. 25, the discrepancy is significantly reduced when the ETS affinities are instead used to compute the average HOMO. The average difference between  $\epsilon_{\text{HOMO}}^{\text{PBE}}$  and  $\epsilon_{\text{HOMO}}^{\text{av.ETS}}$  is just 0.022 a.u. for the 12 molecules, essentially the same as that obtained for the first three systems (when compared to  $\epsilon_{\text{HOMO}}^{\text{av.GS}}$ ). The key conclusion of Table II is that the conventional PBE HOMO energies are almost an order of magnitude closer to the average values (determined using the ground state affinity for systems that do bind an excess electron but the ETS affinity for those that do not) than to the Koopmans values of  $-I^0$ .

Table III presents the equivalent analysis for the LUMO energies. The first column lists the WY LUMO energies denoted as  $\epsilon_{\text{LUMO}}^{\text{WY}}$ . The second column lists LUMO energies from conventional Kohn–Sham calculations using the PBE functional denoted as  $\epsilon_{\text{LUMO}}^{\text{PBE}}$ . The PBE values are all negative, and it is important to note that they barely change when increasingly diffuse functions are added to the basis set. The final four columns list  $\epsilon_{\text{LUMO}}^{\text{av.GS}}$ ,  $\epsilon_{\text{LUMO}}^{\text{av.ETS}}$ ,  $-A^{0,\text{GS}}$ , and  $-A^{0,\text{ETS}}$ . Consistent with Eq. (5), the  $\epsilon_{\text{LUMO}}^{\text{WY}}$  values bear no resemblance to  $-A^{0,\text{GS}}$  and  $-A^{0,\text{ETS}}$ .

For the first three molecules, the  $\epsilon_{\text{LUMO}}^{\text{PBE}}$  values are uniformly below  $-A^{0,\text{GS}}$  by an average of 0.157 a.u. The errors are, on average, approximately equal and opposite to those obtained when comparing the HOMO with  $-I^0$ , resembling the behavior in Eqs. (16) and (17). It follows that the  $\epsilon_{\text{LUMO}}^{\text{PBE}}$  values are reasonably close to  $\epsilon_{\text{LUMO}}^{\text{av.GS}}$ , with a mean absolute difference of just 0.010 a.u. For the remaining 12 molecules, the  $\epsilon_{\text{LUMO}}^{\text{PBE}}$  values are below the  $-A^{0,\text{GS}}$  and  $-A^{0,\text{ETS}}$  values by

TABLE III. LUMO energies compared to  $-A^{0,GS}$  and  $-A^{0,ETS}$ . All quantities are in a.u.

Molecule	$\epsilon_{LUMO}^{WY}$	$\epsilon_{LUMO}^{PBE}$	$\epsilon_{LUMO}^{PBE(AC)}$	$\epsilon_{LUMO}^{B3LYP}$	$\epsilon_{LUMO}^{av,GS}$	$\epsilon_{LUMO}^{av,ETS}$	$-A^{0,GS}$	$-A^{0,ETS}$
Systems that do vertically bind an excess electron								
SO <sub>2</sub>	-0.310	-0.162	-0.161	-0.135	-0.173	...	-0.026	...
Cl <sub>2</sub>	-0.303	-0.155	-0.154	-0.122	-0.163	...	-0.022	...
F <sub>2</sub>	-0.418	-0.213	-0.207	-0.162	-0.223	...	-0.011	...
$ d $ vs $-A^{0,GS}$	0.324	0.157	0.154	0.120				
$ d $ vs $\epsilon_{LUMO}^{av,GS}$	0.157	0.010	0.012	0.047				
Systems that do not vertically bind an excess electron								
H <sub>2</sub> CO	-0.255	-0.098	-0.093	-0.061	-0.129	-0.101	0.000	0.055
C <sub>2</sub> H <sub>4</sub>	-0.179	-0.040	-0.034	-0.009	-0.090	-0.057	0.000	0.066
CO	-0.247	-0.073	-0.070	-0.038	-0.125	-0.092	0.000	0.066
PH <sub>3</sub>	-0.134	-0.023	-0.010	-0.014	-0.074	-0.039	0.000	0.070
H <sub>2</sub> S	-0.166	-0.031	-0.020	-0.019	-0.084	-0.046	0.000	0.077
HCN	-0.202	-0.040	-0.034	-0.010	-0.102	-0.059	0.000	0.085
HCl	-0.194	-0.040	-0.033	-0.025	-0.098	-0.037	0.000	0.121
CO <sub>2</sub>	-0.180	-0.032	-0.015	-0.019	-0.092	-0.022	0.000	0.140
NH <sub>3</sub>	-0.166	-0.026	+0.011	-0.017	-0.083	+0.020	0.000	0.206
HF	-0.213	-0.036	+0.029	-0.024	-0.109	+0.001	0.000	0.220
H <sub>2</sub> O	-0.191	-0.034	+0.012	-0.023	-0.096	+0.022	0.000	0.235
CH <sub>4</sub>	-0.158	-0.013	+0.025	-0.007	-0.079	+0.064	0.000	0.287
$ d $ vs $-A^{0,GS}$	0.191	0.041	0.032	0.022				
$ d $ vs $-A^{0,ETS}$	0.326	0.176	0.155	0.158				
$ d $ vs $\epsilon_{LUMO}^{av,GS}$	0.094	0.056	0.077	0.075				
$ d $ vs $\epsilon_{LUMO}^{av,ETS}$	0.162	0.026	0.019	0.036				

averages of 0.041 and 0.176 a.u., respectively. The latter errors—but not the former—are approximately equal and opposite to those obtained when comparing the HOMO with  $-I^0$ , now resembling the behavior in Eqs. (19) and (20). It follows that the  $\epsilon_{LUMO}^{PBE}$  values are closer to  $\epsilon_{LUMO}^{av,ETS}$  than to  $\epsilon_{LUMO}^{av,GS}$ ; the mean absolute differences are 0.026 and 0.056 a.u., respectively.

The need to use the ETS affinities, rather than the ground state values, is less pronounced for the LUMO energies than for the HOMO energies. The reason for this can be traced to a notable discrepancy between the  $\epsilon_{LUMO}^{PBE}$  and  $\epsilon_{LUMO}^{av,ETS}$  values in Table III. Namely, the former values are all negative, whereas the latter become *positive* toward the bottom of the table. As noted in Sec. I, it is well established that the exchange-correlation potentials of local functionals such as PBE break down in asymptotic regions. This leads to errors in high-lying virtual orbitals, but it may also have an effect on LUMOs that are sufficiently diffuse. In order to investigate whether this is the origin of the sign discrepancy, we have improved the PBE potential by applying an AC using the scheme of Tozer and Handy.<sup>18</sup> Standard connection parameters of  $\alpha=3.0$  and  $\beta=4.0$  are used, together with the PBE ionization potential. The HOMO and LUMO energies from the asymptotically corrected calculations, denoted as  $\epsilon_{HOMO}^{PBE(AC)}$  and  $\epsilon_{LUMO}^{PBE(AC)}$ , are listed in Tables II and III, respectively.

The HOMO energies in Table II are barely affected by the AC (i.e.,  $\epsilon_{HOMO}^{PBE} \approx \epsilon_{HOMO}^{PBE(AC)}$ ) because the compact nature of these orbitals makes them insensitive to the asymptotic potential. For the LUMO energies in Table III, the effect of the AC depends on the position in the table. Near the top of the table (positive affinities or small magnitude ETS affinities), the LUMO energies are not affected significantly, indi-

cating that the orbitals are again reasonably compact. By contrast, for systems near the bottom of the table (large magnitude ETS affinities), the AC has a significant effect, indicating that these orbitals are more diffuse, making them prone to errors due to the breakdown of the asymptotic potential. It is striking that for these molecules, the AC leads to positive LUMO energies, which are consistent with the  $\epsilon_{LUMO}^{av,ETS}$  values, confirming our view that the discrepancy arises due to asymptotic breakdown. For the 12 molecules that do not bind an excess electron, the  $\epsilon_{LUMO}^{PBE(AC)}$  values are now notably closer to  $\epsilon_{LUMO}^{av,ETS}$  than to  $\epsilon_{LUMO}^{av,GS}$ ; the mean absolute differences are 0.019 and 0.077 a.u., respectively. The need to use the ETS affinities is therefore recovered, consistent with the HOMO observations.

It is important to stress that for all 15 molecules the PBE and PBE(AC) LUMO orbitals are bound (in the limit of a complete basis set), even though some of the latter have positive energies. This is because the LUMO energies are always below their respective asymptotic potentials in the Kohn–Sham equations. For PBE, the asymptotic potential is zero, but for PBE(AC) it takes the positive value,<sup>18</sup>

$$\lim_{r \rightarrow \infty} v_{XC}^{PBE(AC)}(\mathbf{r}) = \epsilon_{HOMO}^{PBE(AC)} + I^{PBE}, \quad (22)$$

allowing for the possibility of bound orbitals with positive energies. This is illustrated in Fig. 1, which plots the PBE and PBE(AC) exchange-correlation potentials along the principal axis of the HF molecule; the two horizontal lines represent the PBE and PBE(AC) LUMO energies. Despite the positive orbital energy, the PBE(AC) LUMO is actually more strongly bound than the PBE one in the sense that it lies further below the asymptotic potential. We note that the

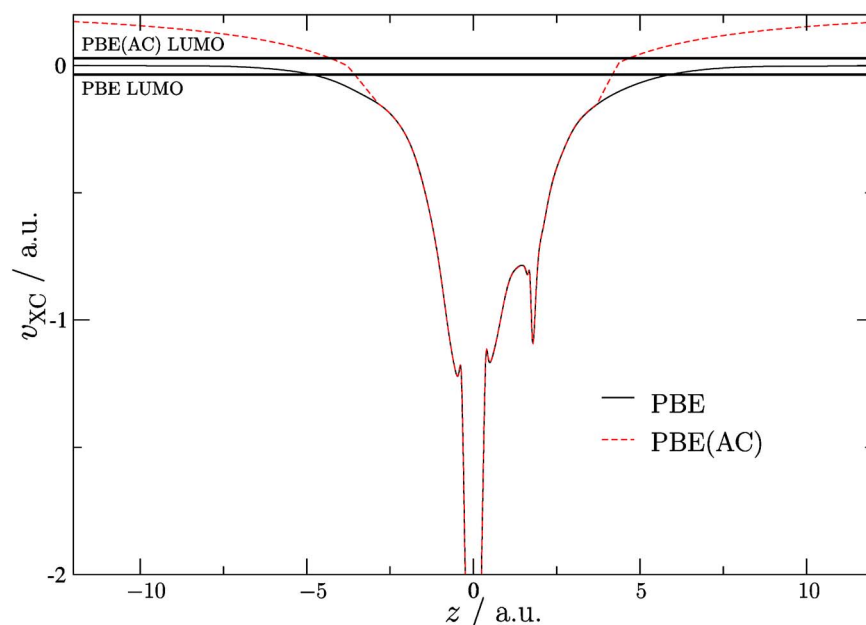


FIG. 1. (Color online) PBE and PBE(AC) exchange-correlation potentials in the HF molecule plotted along the bond axis. The horizontal lines indicate the LUMO orbital energies.

AC has the added benefit that it shifts the discretized continuum solutions away from the LUMO.<sup>47</sup>

The WY data also provide a second approach for correcting the LUMO energy. We can define a new LUMO energy that lies above the PBE HOMO energy by the same amount as the WY LUMO energy lies above the WY HOMO energy. In other words, we can correct the LUMO energy such that the HOMO-LUMO gap equals the accurate WY value,

$$\epsilon_{\text{LUMO}}^{\text{WY/PBE}} = \epsilon_{\text{HOMO}}^{\text{PBE}} + \epsilon_{\text{LUMO}}^{\text{WY}} - \epsilon_{\text{HOMO}}^{\text{WY}}. \quad (23)$$

Values of  $\epsilon_{\text{LUMO}}^{\text{WY/PBE}}$  (not presented) are rather close to the  $\epsilon_{\text{LUMO}}^{\text{PBE(AC)}}$  values and—importantly—they also become positive for the final four molecules.

The results of Tables II and III are consistent with our earlier studies<sup>20,23–25</sup> and with the theoretical discussion of Sec. I—local functional frontier orbital energies exhibit a near-average behavior (provided that an AC is applied for particularly diffuse LUMOs). For systems that do bind an excess electron, the orbital energies resemble those in Eqs. (16) and (17); for those that do not bind, they more closely resemble those in Eqs. (19) and (20). In all cases, typical discrepancies are 0.02 a.u. The results clearly illustrate why the unconventional affinity in Eq. (13) provides an estimate of the positive ground state affinity in the former case but the negative ETS affinity in the latter.

We suggest that the need to use the ETS affinity—rather than the ground state affinity—simply reflects the fact that the LUMO of the neutral is a *bound* orbital. Electron addition into this orbital more closely resembles the ETS situation, where the electron is temporarily captured in a localized orbital, than the ground state situation, where the excess electron enters a continuum state.

### C. Exchange-correlation potentials from a local functional

The analysis of Sec. II B demonstrates that the HOMO and LUMO energies from PBE(AC) (and, for the most part, PBE) exhibit a near-average behavior. This observation, together with the general success of local functionals, implies that the PBE(AC) potential must also be near average in regions relevant to the HOMO and LUMO. We now demonstrate this explicitly for two representative systems.

The WY potential  $v_{\text{XC}}^{\text{WY}}(\mathbf{r})$  is our best estimate to the exact  $v_{\text{XC}}^-(\mathbf{r})$  [Eq. (14)]. For systems that bind an excess electron, the PBE(AC) potential should therefore lie approximately midway between  $v_{\text{XC}}^{\text{WY}}(\mathbf{r})$  and  $(v_{\text{XC}}^{\text{WY}}(\mathbf{r}) + \Delta_{\text{XC}}^{\text{GS}})$ . This is vividly illustrated in Fig. 2(a), which plots the potentials along the bond axis of the F<sub>2</sub> molecule. The need to asymptotically correct the potential to maintain the average behavior at large distances is particularly pronounced, although this has a minimal effect on the LUMO energy for this system. (We observe that the WY potential exhibits small unphysical undulations at regions away from the nuclei. These may reflect the use of Gaussian basis functions in the calculation,<sup>48</sup> or they may arise due to the numerics of the WY approach. Using the value of  $\lambda$  based on the reciprocal slope actually increases the size of these undulations. The HOMO-LUMO gaps are not sensitive to these features—further increasing  $\lambda$  or using the primary orbital basis set eliminates them with minimal effect on the gap, but these calculations have the disadvantage that they also reduce the true physical intershell structure.)

For systems that do not bind an excess electron, the PBE(AC) potential should lie approximately midway between  $v_{\text{XC}}^{\text{WY}}(\mathbf{r})$  and  $(v_{\text{XC}}^{\text{WY}}(\mathbf{r}) + \Delta_{\text{XC}}^{\text{ETS}})$ . This is again clearly illustrated in Fig. 2(b), which presents the potentials for the HF molecule. Note that the WY potential only exhibits a weak feature at the position of the H atom (at  $z=1.73$  a.u.),



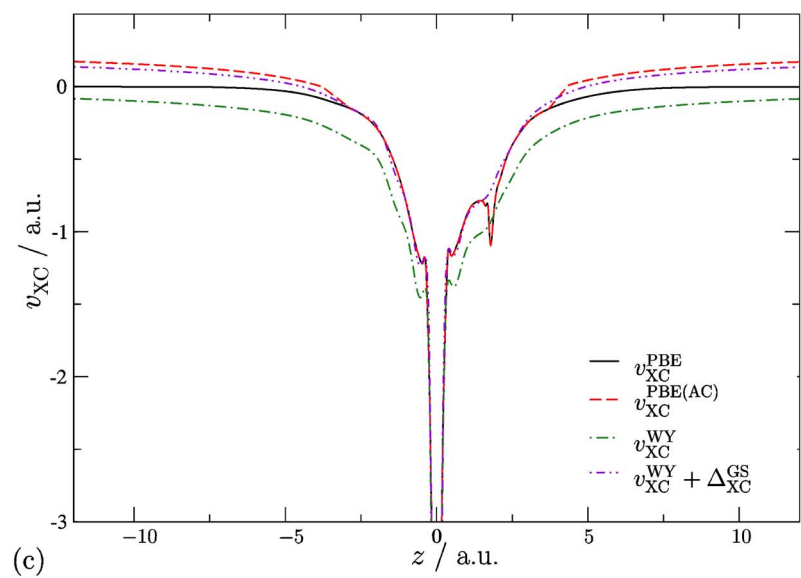
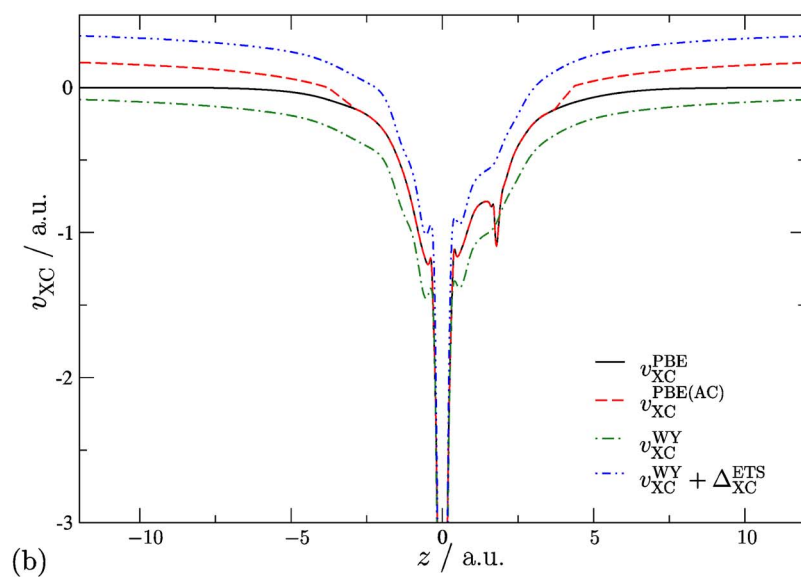
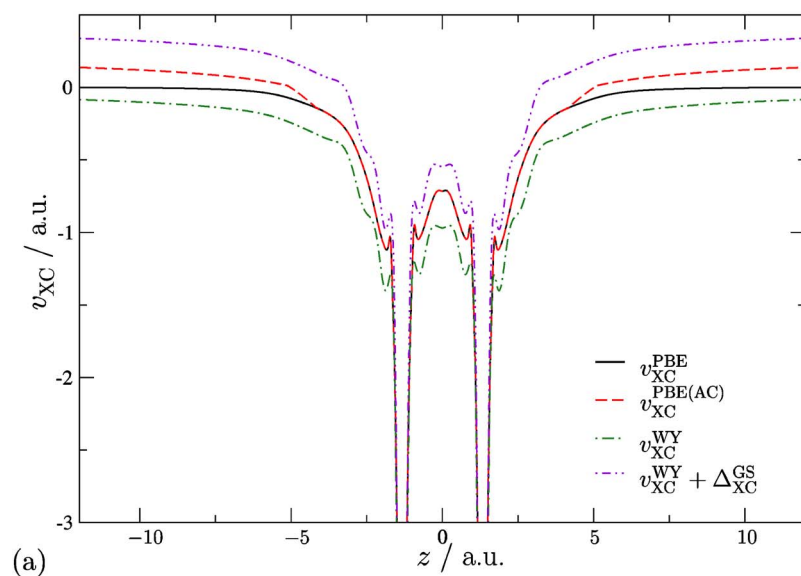


FIG. 2. (Color online) Exchange-correlation potentials plotted along the bond axis. (a)  $F_2$  using  $\Delta_{XC}^{GS}$ , (b) HF using  $\Delta_{XC}^{ETS}$ , and (c) HF using  $\Delta_{XC}^{GS}$ .

consistent with an earlier work.<sup>49</sup> By contrast, PBE(AC) has a much sharper feature, reflecting the known failure of GGA potentials at nuclei.<sup>50</sup> To further highlight the importance of using the ETS affinity for these systems, Fig. 2(c) replaces  $\Delta_{XC}^{ETS}$  with  $\Delta_{XC}^{GS}$  in the electron abundant potential. The PBE(AC) potential no longer resembles the average potential. The similarity of the PBE(AC) potential and  $(v_{XC}^{WY}(\mathbf{r}) + \Delta_{XC}^{GS})$  simply reflects the fact that the PBE(AC) HOMO is numerically similar to the WY HOMO-LUMO gap.

#### D. Orbital energies from a hybrid functional

Most calculations in the chemical literature use hybrid functionals such as B3LYP,<sup>51–54</sup> which combine a GGA term with a fraction of orbital exchange. It is therefore pertinent to mention B3LYP HOMO and LUMO energies. Tables II and III present the conventional B3LYP orbital energies denoted  $\epsilon_{HOMO}^{B3LYP}$  and  $\epsilon_{LUMO}^{B3LYP}$ .

For all the systems, the  $\epsilon_{HOMO}^{B3LYP}$  values lie below  $\epsilon_{HOMO}^{PBE}$ , and so the agreement with  $-I^0$  is slightly improved. For the first three molecules, the agreement with  $\epsilon_{HOMO}^{av,GS}$  is less marked than it is with PBE. For the remaining ones, the mean absolute differences between  $\epsilon_{HOMO}^{B3LYP}$  and  $\epsilon_{HOMO}^{av,GS}$  or  $\epsilon_{HOMO}^{av,ETS}$  are essentially the same; there is no clear preference, and it depends on the particular molecule. For all systems, the  $\epsilon_{LUMO}^{B3LYP}$  values lie above  $\epsilon_{LUMO}^{PBE}$ . For the first three molecules, the agreement with  $\epsilon_{LUMO}^{av,GS}$  is much less marked than it is with PBE. For the remaining molecules, the  $\epsilon_{LUMO}^{B3LYP}$  more closely resemble  $\epsilon_{HOMO}^{av,ETS}$  than  $\epsilon_{HOMO}^{av,GS}$ , but the agreement is again less marked than it is with PBE.

The situation with B3LYP is therefore less clear than with PBE, and this can be traced to the nature of the orbital equations in conventional implementations of hybrid functionals. They are obtained by minimizing the energy with respect to the orbitals rather than the density. The exchange-correlation operator is therefore nonmultiplicative, meaning that there is no well-defined exchange-correlation potential. It follows that unlike the PBE results, the B3LYP results cannot be understood in terms of the mathematical analysis in Sec. I. The fact that the B3LYP HOMO and LUMO are uniformly below and above the PBE values means that electron affinities from Eq. (13) are still reasonable, although, as noted in Ref. 9, they are less accurate than they are with PBE.

The rigorous way to perform B3LYP calculations is to use the optimized effective potential<sup>55,56</sup> approach, which minimizes the energy with respect to the density. Such calculations, which are beyond the scope of the present study, would yield (on the electron deficient side) HOMO energies close to the conventional B3LYP values but LUMO values that differ significantly from the conventional B3LYP ones; see Ref. 13 for a discussion of this point. The B3LYP LUMO values would be such that the B3LYP HOMO-LUMO gap is close to the WY gaps (slightly larger than the PBE gaps). In effect the B3LYP HOMO and LUMO energies would both be shifted down from the PBE values. The application of Eq. (13) would be inappropriate, leading to significant errors.

#### E. Discussion in terms of $E$ versus electron number

Recent studies<sup>6,7,14</sup> have considered the variation in the DFT electronic energy as a function of electron number. We close by considering the results of the present study in this context. Figure 3(a) presents a schematic plot of energy versus electron number for a molecule that binds an excess electron. The points labeled  $E_{N-1}^0$ ,  $E_N^0$ , and  $E_{N+1}^0$  are the exact ground state electronic energies of the  $N-1$  (cation),  $N$  (neutral), and  $N+1$  (anion) electron systems. Following Ref. 1, the exact ground state energy varies linearly between these values. The vertical lines labeled  $I^0$  and  $A^{0,GS}$  represent the exact vertical ionization potential and electron affinity, respectively. (All vertical lines in Fig. 3 represent positive quantities). The change in the slope from  $-I^0$  to  $-A^0$  as the electron number increases through  $N$  arises due to the discontinuous behavior of the exact exchange-correlation and kinetic components. Local functionals such as GGA yield reasonable estimates for the ground state energies of systems with integer numbers of electrons but give energies that are significantly too low for noninteger. The dashed curve illustrates this convex behavior. The departure from linearity has been termed a many-electron self-interaction error.<sup>6,7,14</sup> For the clarity of the plot, the total energies of the three integers from the local functional have been set equal to the exact energies. In practice these energies will not be this close to the exact values. However the differences between them (the ionization potential and the electron affinity) are usually in good agreement. We do not consider the influence of the AC in this figure, as the associated energy functional is not known.

From Janak's theorem,<sup>19</sup> the initial slopes of the local functional curve on the electron deficient and electron abundant sides of  $N$  are the HOMO and LUMO energies of the  $N$ -electron system, respectively. These initial slopes are marked on the figure, allowing the negative of the orbital energies to be represented by vertical lines. (The difference between the initial slopes is barely evident in the figure because the HOMO and LUMO energies are of similar magnitude). The fact that  $-\epsilon_{HOMO}^{local} < I^0$  and  $-\epsilon_{LUMO}^{local} > A^{0,GS}$  can therefore be attributed to the convexity of the curve.<sup>13</sup> We define positive differences, marked  $\lambda_-$  and  $\lambda_+$  on the figure, by

$$\epsilon_{HOMO}^{local} = -I^0 + \lambda_- \quad (24)$$

and

$$\epsilon_{LUMO}^{local} = -A^{0,GS} - \lambda_+. \quad (25)$$

Tables II and III demonstrate that local functional HOMO and LUMO energies are close to the average values in Eqs. (16) and (17). Comparing Eqs. (24) and (25) with Eqs. (16) and (17), respectively, leads to the approximate equality

$$\lambda_- \approx \lambda_+ \approx \frac{\Delta_{XC}^{GS}}{2}. \quad (26)$$

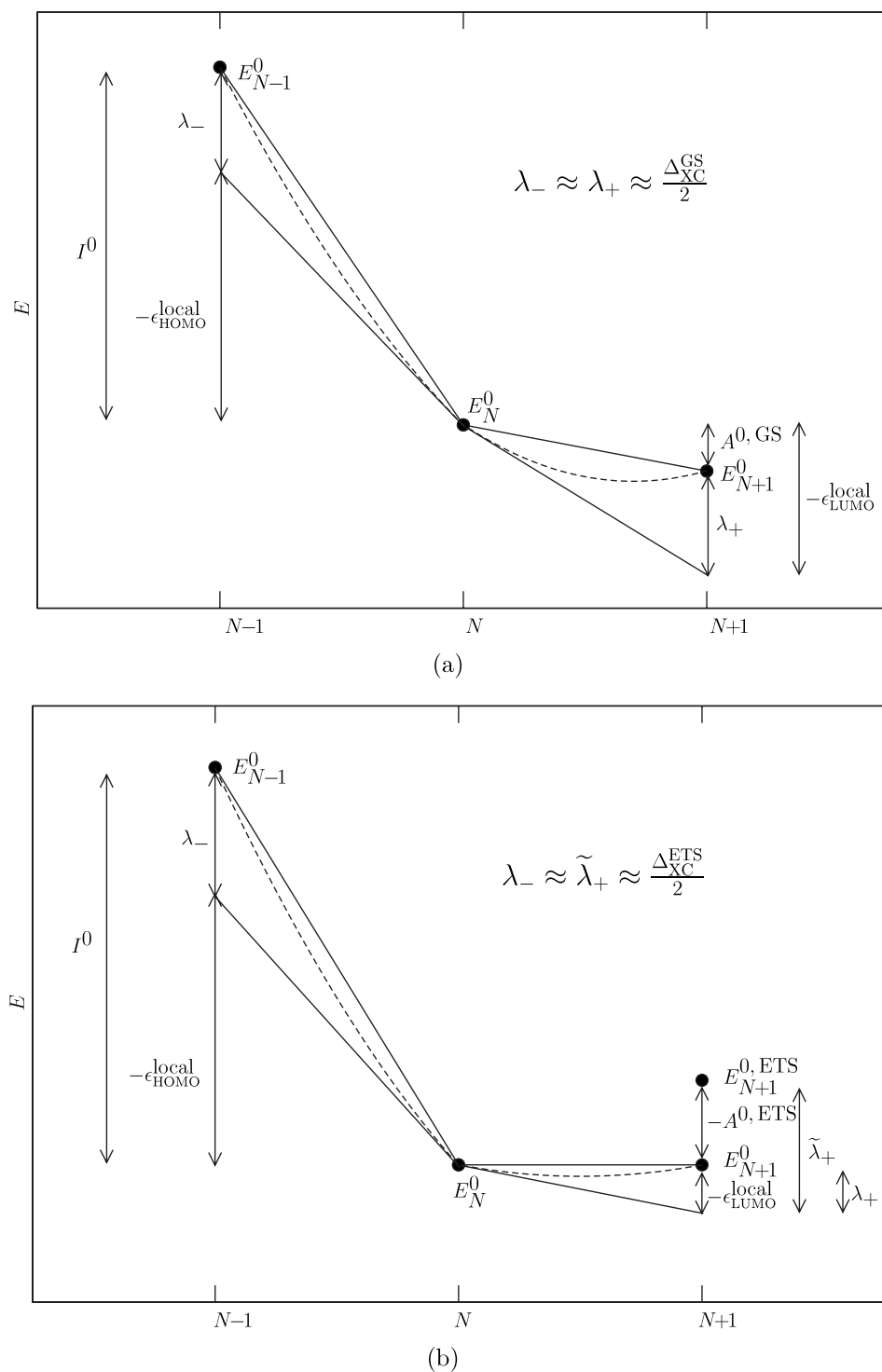


FIG. 3. Schematic plots of electronic energy vs electron number for systems that (a) do bind and (b) do not bind an excess electron. The solid line connecting the energy points is the exact ground state energy; the dashed curve represents a typical local functional behavior, with the integer energies set equal to the exact values for clarity. See text for full details.

The average behavior therefore manifests itself as a symmetry between the electron deficient and electron abundant sides of the figure. In terms of this notation, the unconventional affinity in Eq. (13) takes the form

$$A^{TDP} = A^{0,GS} + (I^0 - I^{local}) + (\lambda_+ - \lambda_-). \quad (27)$$

In terms of Fig. 3(a), it is therefore the approximate equality  $\lambda_- \approx \lambda_+$ , together with the fact that  $I^{local} \approx I^0$ , that leads to approximate ground state affinities from Eqs. (27) and (13) for systems that do bind an excess electron,

$$A^{TDP} \approx A^{0,GS}. \quad (28)$$

Figure 3(b) presents the analogous plot for a system that does not bind an excess electron. The ground state energy of the anion is now identical to that of the neutral. The energy labeled  $E_{N+1}^{0,ETS}$  is the energy of the temporary anion, consistent with the ETS affinity  $A^{0,ETS}$ , the negative of which is represented by a vertical line. The difference between the initial slopes of the local functional curve is now much more evident because the HOMO and LUMO energies are very different. If we continue to define  $\lambda_+$  and  $\lambda_-$  using Eqs. (24) and (25), then  $\lambda_+$  becomes identical to the negative of the LUMO energy because  $A^{0,GS} = 0$ . For systems that do not

bind, the LUMO energy is a small negative value, and so  $\lambda_+ < \lambda_-$ , as shown in the figure. It follows that Eq. (27) yields a negative affinity.

It is therefore natural to define the alternative quantity,  $\tilde{\lambda}_+$ ,

$$\epsilon_{\text{LUMO}}^{\text{local}} = -A^{0,\text{ETS}} - \tilde{\lambda}_+, \quad (29)$$

which is also shown in Fig. 3(b). Tables II and III show that local functional HOMO and LUMO energies are close to the average values in Eqs. (19) and (20). Comparing Eqs. (24) and (29) with Eqs. (19) and (20), respectively, leads to the approximate equality

$$\lambda_- \approx \tilde{\lambda}_+ \approx \frac{\Delta_{\text{XC}}^{\text{ETS}}}{2}. \quad (30)$$

In this case, the unconventional affinity takes the form

$$A^{\text{TDP}} = A^{0,\text{ETS}} + (I^0 - I^{\text{local}}) + (\tilde{\lambda}_+ - \lambda_-). \quad (31)$$

In terms of Fig. 3(b), it is therefore the approximate equality in Eq. (30), together with the fact that  $I^{\text{local}} \approx I^0$ , that leads to approximate negative ETS affinities from Eqs. (27) and (13) for systems that do not bind an excess electron,

$$A^{\text{TDP}} \approx A^{0,\text{ETS}}. \quad (32)$$

### III. CONCLUSIONS

Following a brief summary of earlier relevant studies, we have investigated DFT closed-shell orbital energies, paying attention to the role of the integer discontinuity in the exact exchange-correlation potential. *Ab initio* electron densities and accurate vertical ionization potentials and electron affinities have been used to calculate accurate average orbital energies, i.e., the energies associated with an exchange-correlation potential that averages over a constant jump of magnitude  $\Delta_{\text{XC}}$  [Eq. (6)] in the accurate potential. For systems that do bind an excess electron, there is no choice of electron affinity in the average energy calculation—the positive ground state value must be used. For systems that do not bind, however, there are two possible affinities—the zero ground state or the negative ETS value.

HOMO energies from the PBE local functional are almost an order of magnitude closer to the average values than to the Koopmans values, with typical discrepancies of just 0.02 a.u. For systems that do not bind an excess electron, this level of agreement is only achieved when the negative ETS affinity is used to calculate the average energy; it degrades notably when the zero ground state affinity is instead used. Analogous observations are made for the PBE LUMO energies, although the need to use the ETS affinities is less pronounced for systems where the ETS values are very negative. The application of an AC recovers the preference, leading to positive LUMO energies (but bound orbitals) for these systems, consistent with the behavior of the average energies. Overall, the asymptotically corrected LUMO energies typically agree with the average values to within 0.02 a.u., comparable to that observed with the HOMOs.

Our results are consistent with earlier work and with the theoretical analysis of Sec. I, providing numerical support

for the view that local functionals exhibit a near-average behavior based on a constant jump of magnitude  $\Delta_{\text{XC}}$  (providing an AC is applied for particularly diffuse LUMOs). For systems that do bind an excess electron, the orbital energies resemble those in Eqs. (16) and (17); for those that do not bind, they more closely resemble those in Eqs. (19) and (20). The results clearly illustrate why the unconventional affinity in Eq. (13) provides an estimate of the positive ground state affinity in the former case but the negative ETS affinity in the latter. The latter seems to reflect the fact that the LUMO of the neutral is a bound orbital, and so electron addition more closely resembles the ETS situation. The results are also consistent with the charge-transfer excitation energy analysis in Ref. 10. The near-average behavior of the exchange-correlation potential has been explicitly illustrated for selected systems.

We have also considered hybrid functional orbital energies, but these cannot be simply understood in terms of the theoretical analysis in Sec. I due to the non-Kohn–Sham nature of the orbital energies used in standard implementations. Finally, given the current interest in the variation in the electronic energy as a function of electron number, we have discussed the results of the present study in this context.

The nature of DFT orbital energies is of great importance in chemistry; the present study contributes to the understanding of these quantities.

### ACKNOWLEDGMENTS

The authors thank Michael J. G. Peach, Aron J. Cohen, Trygve Helgaker, John Perdew, and Paul Ayers for helpful discussions. A.M.T. gratefully acknowledges support from the Norwegian Research Council through the CeO Centre for Theoretical and Computational Chemistry (Grant No. 179568/V30) and postdoctoral research funding (Grant No. 171185).

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